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Silver Nanoparticle-Assisted Photocurrent Generation in Polythiophene-Fullerene Thin Films

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1. Introduction

Polythiophene derivatives such as poly (3-hexylthiophene) (P3HT) and fullerene derivatives such as [6,6]-phenyl C_{61}-butyric acid methylester(PCBM) have been used as a couple of photoelectric conversion pair for organic solar cells[1,2]. In order to increase the photo conversation efficiency, the film with low optical reflectance and high excitation efficiency is desired. [3].

Recently, surface plasmon resonance (SPR) of the nanostructures of silver or gold has been utilized to enhance the absorption efficiency in silicon solar cells [4~5], due to their characteristic optical phenomena such as enhancement of induced absorption and emission. However, to the best of our knowledge, there is no useful approaches for the introduction of plasmonic metal nanoparticles which is chemically prepared in solution have not been developed. Since chemically-synthesized metal nanoparticles offer well defined shapes with narrow size distribution, they are advantageous for their incorporation in a specified position between the electrodes of the solar cell and for characterization of the effects of SPR. Thus, they can be advantageous for use in organic solar cells.

Here, we report an approach for the introduction of chemically-synthesized silver nanoparticles in photoelectric conversion films, intended for use as the films of organic solar cells. The method includes the electrostatic layer-by-layer adsorption process of the layer of silver nanoparticles (AgPs) on the surface of ITO glass [6]. We also have investigated the influence of the AgPs layer on the photocurrent generate from the films consisting of P3HT and PCBM or P3HT alone.

2. Experimental Procedure

Fabrication procedure of AgPs and P3HT-PCBM films is shown in Fig.1.

A Clean ITO electrode was immersed into PEI (polyethyleneimine) solution for 30min at 30℃, and then immersed into an aqueous AgPs solution [6] for 10h at 30℃, then a chlorobenzen solution of P3HT (0.2mg/L) or of P3HT:PCBM(1:1) (0.2mg/L each) were spin-coated on the surface of AgPs layer at 2000rpm without annealing.

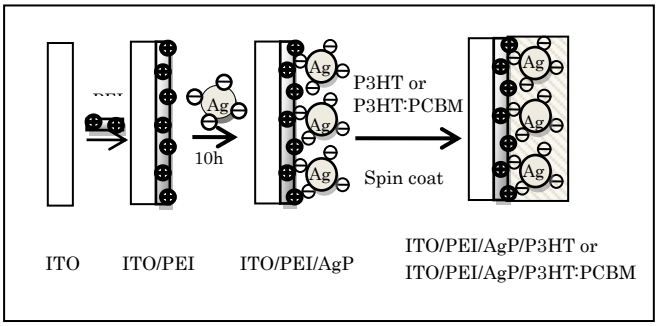

Fig. 1 Schematic illustration for fabrication Polythiophene-Fullerene films on AgP modified ITO

We have fabricated four kinds of films in this study: S1 for ITO/PEI/AgPs/P3HT; S2 for ITO/PEI/AgPs/P3HT: S3 for PCBM; ITO/PEI/P3HT; S4 for ITO/PEI/P3HT:PCBM respectively.

Absorption spectrum (ASCO V-670) and scanning microscope (SEM) images (Hitachi S-5000) were carried out to identify the feature of AgPs layers. Photocurrents were carried out with our three-electrode photo-electrochemical cell.

3. Results and Discussion

Fig. 2 shows absorption spectrum of S1, S2, S3 and S4.

Board absorption bands around 420 nm of S1 and S2 can be assigned to plasmon bands of isolated AgPs, while broad bands around 600~800nm to plasmon bands of AgPs aggregates [7]. The thickness of spin-coated film was evaluated by dissolving the spin-coated sample in chlorobenzene. The film thickness of P3HT was several times higher than that of P3HT:PCBM, in spite of the presence or absence of AgPs. Probably, the presence of PCBM in the polymer solution increased the spreading property.

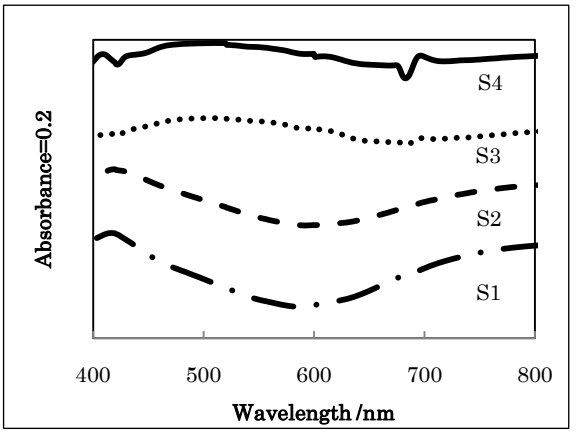

Fig. 2 (a) Absorption spectra of S1~S4

Figure 3 shows SEM images of AgPs layer of S1 and S2. AgPs are indicated as white spots. From SEM images the size of AgPs is defined to be 31~81 nm, and the fractional coverage for S1 and S2 are 45.7 and 54.2% respectively. In addition, AgPs were considerably aggregated. Thus, it is quite Reasonable that the spectra show broad plasmon bands dure to plasmon coupling among AgPs

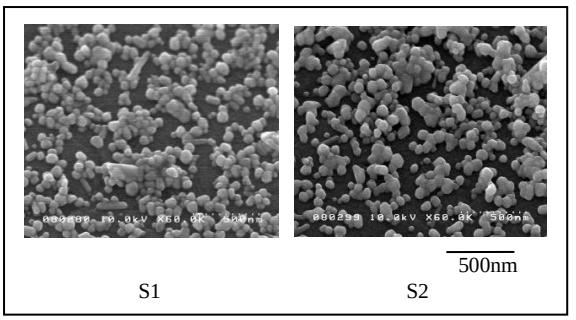

Fig.3 SEM images of AgP layer of S1 and S2

Fluorescence excitation spectra of the films (monitored at 637nm) were measured to investigate the effects of AgPs on the films. The results imply that the incorporation of AgPs in these films enhances the population of excited states of P3HT. Especially, the fluorescence of S4 is substantially enhanced as compared with other three films.

Photocurrent action spectra of the four films were measured under the identical experimental condition. The results are shown in Fig.4.

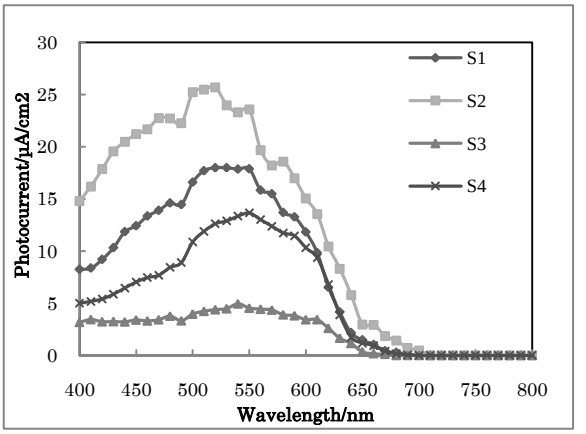

Fig.4 Photocurrent action spectra of S1~S4

Since these film thicknesses of four samples are somewhat different among them, we have evaluated the quantities of the spin-coated P3HT, from absorption spectroscopy as described above. Even after consideration of the film thickness, the films with AgPs gave appreciably lager photocurrent responses as compared with those of the corresponding films without AgPs.

Accordingly, it was strongly suggested that the incorporation of chemically-synthesized AgPs in photoelectric conversion films were successful, and AgPs enhanced the photocurrent responses.

4. Conclusions

We have successfully incorporated chemically-synthesized AgPs in the organic thin film consisting of P3HT and PCBM. In this study, we incorporated AgPs just on the surface of the ITO electrode, as a preliminary examination. AgPs showed clear enhancement of photocurrent responses. It's most probably due to the effects of SPR. Thus, it is quite important to find out the best position to be incorporated in the films. Further studies are now in progress.

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